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First study of nano-composite scintillators under alpha irradiation

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We demonstrate that nano-composite materials based on semiconductor quantum dots have great potential for radiation detection via scintillation. While quantum dots and laser dyes both emit in the visible range at room temperature, the Stokes shift of the dyes is significantly larger. The scintillation output of both systems was studied under alpha irradiation and interpreted using a combination of energy-loss and photon transport Monte Carlo simulation models. The comparison of the two systems, which allows the quantification of the role played by the Stokes shift in the scintillation output, opens up exciting possibilities for a new class of scintillators that would take advantage of the limitless assembly of nano-crystals in large, transparent, and sturdy matrices.

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Although both the synthesis and characterization of quantum dots have been developed for more than a decade,^{1,2} the applications explored to date seem to have focused on tagging,³ chemical and biological sensing,⁴ and lasing applications.⁵ The interest generated by quantum dots in both academic and industrial research communities comes from the fact that the optical properties of these materials are directly tied to their composition, size, and geometry, therefore allowing the engineering of key parameters such as emission wavelength and quantum efficiency.

Standard gamma-ray detection technology relies on cooled germanium detectors (0.2 % energy resolution at 1.33 MeV)⁶⁻⁸ and on scintillating crystals such as sodium iodide (7 % energy resolution at 662 keV).⁹ The main problem associated with the former is the necessity to cool and stabilize the detector at a temperature near liquid nitrogen to reduce thermal noise. The main problem associated with the latter is its poor energy resolution and the limited choice of photon transducers (photomultipliers).

The use of nano-composite materials could potentially lead to a new class of scintillators that would operate at room temperature, and more importantly, that would not rely on crystal growth, but on the assembly of nanometer-sized crystals in a transparent and sturdy matrix. Moreover, scintillator materials have output wavelengths in the UV and blue (the most commonly used scintillator, sodium iodide, emits at 460 nm), wavelengths at which the quantum efficiency of photomultiplier tubes (PMT) is below 25 %.¹⁰ This means that, even in an ideal situation, only ¼ of the photons produced in the scintillator material are detected. The use of quantum dots as a scintillator medium would allow fine tuning of the output wavelength in the visible range and therefore, the use of avalanche

photodiodes (APD) with quantum efficiencies up to 70%.¹¹ The visible band gap of quantum dots would ensure both high photon output and efficient photon counting.

To the best of our knowledge, only one preliminary example of nano-crystal-based scintillator has been reported to date.¹² In this work, core/shell (CdSe)ZnS quantum dots were embedded into a thin lithiated sol-gel matrix, characterized optically, and tested with an alpha source. Unfortunately, no conclusion can be drawn from this publication since the only scintillation spectrum presented was not corrected from the background radiation. In this letter, we demonstrate the ability of quantum dots to convert alpha radiation into visible photons, compare the scintillation output of quantum dots and laser dye molecules, and interpret the results using a combination of energy-loss and photon transport models. This set of data allows us to discuss the limitations of basic quantum dots for gamma-radiation application that require large volumes of scintillator material, and to suggest a new route to solve these issues.

Porous VYCOR® was purchased from Advanced Glass and Ceramics (Holden, MA) in 1/16 inch thick sheets. As received, the material is constituted of an array of interconnected pores with a diameter of 4 nm and is opalescent. The porous glass matrix was slowly dissolved for 4 days in an aqueous solution containing 1 % of hydrofluoric acid and 20 % of ethanol per volume, rinsed in ethanol, and dried in air. The purpose of this step was to slightly enhance the pore size and to obtain a clear matrix. SEM top views of the material recorded after etching, cleaning, and drying without applying any conductive coating on the sample surface (see Fig.1(a)) revealed an average pore diameter in the 10-20 nm range. The absorption curve of the same material shows very good transparency in the visible range (see Fig.1(b)). Porous glass constitutes a matrix of

choice for scintillation applications because it is made of a succession of nanometer-sized cavities that can hold guest molecules while separating them from each other, therefore preventing self-quenching effects. In addition, it is sturdy, inert, and transparent.

CdSe/ZnS core shell quantum dots with a luminescence output at 540 nm were purchased from Evident Technologies (Troy, NY) and suspended in toluene at a concentration of 10 mg / mL. Rhodamine B laser dye was purchased from Sigma-Aldrich (Milwaukee, WI) and suspended in methanol at a concentration of 0.5 mM. The dry ‘thirsty’ porous glass pieces were immersed in the solutions of dots or dyes for 48 H with continuous stirring in order to allow homogeneous diffusion of the guest molecules into the nano-porous host matrix. They were then let to dry in order to evaporate the solvent.

Absorbance spectra of the samples were recorded using a UV-vis spectrometer (Cary 100, Varian Inc.) and emission spectra were recorded using a fluorimeter fitted with an optic fiber (Cary Eclipse, Varian Inc.). The spectra as well as pictures of the devices are presented in Fig.2. Although both quantum dots and laser dyes present similarities such as their tunable absorption and emission spectra in the visible range, one noticeable difference is that laser dye molecules have an inherent Stokes shift (shift between absorption and emission wavelength) due to vibrational energy levels while quantum dots do not.

An alpha source ($^{243-244}\text{Cm}$, 0.2 μC) was placed in contact with one side of the 1/16 inch thick porous glass sample and a PMT (model R1924A from Hamamatsu) probing a 1.5 cm diameter area rested directly on the other side to count visible photons coming out of the material. Photons coming out of the nano-composite material samples under alpha irradiation were integrated for 10 H with an amplifier and a multi-channel analyzer.

Figure 3 shows the scintillation output recorded with the $^{243-244}\text{Cm}$ source, through the dot and dye samples. The data presented on Fig.3 shows that the quantum dot system does convert the alpha radiation into visible photons, but that the scintillation output of the laser dye system is significantly higher, showing partial energy resolution of the $^{243-244}\text{Cm}$ source.

In order to specifically understand the role played by the Stokes shift on the energy resolution for both dye and dot systems, as well as to account for the wavelength mismatch between the emission of the sample and the optimal detection of the PMT, we performed simulations using a combination of TRIM and DETECT 2000 programs in history mode.^{13,14} Photons generated at the source/sample interface traveled to the PMT surface which was located on the opposite side of the sample. The history was analyzed and the energy deposition and light transport were simulated while accounting for properties of the scintillator media such as the wavelength-dependent absorption and emission coefficients of the emitters (dot or dye), the nature of the matrix (reflectivity, index of refraction, scattering length, absorption length), and the scintillation decay times.

The wavelength-dependent quantum efficiency of the PMT provided by the Hamamatsu specification sheet was entered into the simulation code. We found that in our un-optimized experimental conditions, about 4.1 % of the photons generated in the dye system were amplified by the PMT, and that 0.4 % were amplified for the dot system. Replacing the PMT, which only has a quantum efficiency of 4 % in the green, by an APD, which has a maximum quantum efficiency of 70 %, would lead to an improvement

of these values by an order of magnitude (38 % of the photons amplified for the dye system and 3.6 % for the dot system).

Many other factors contribute to the observed energy resolution¹⁵ such as the intrinsic properties of the scintillator and the transport efficiency of the photons. For an ideal scintillator, the energy resolution R , is given by: $R = (\Delta E/E)_{\text{fwhm}} = 2.35 \cdot ((1+v(M))/(N \cdot p))^{1/2}$, where N is the average number of photons generated at a given energy E , $v(M)$ is variance in the multiplication factor of the PMT, and p is the average transport efficiency.¹⁵ For a typical 10 stages PMT¹⁶ with a gain of $2 \cdot 10^6$, $v(M)$ is approximately 0.08. For the dye system, we fitted the experimental peak with a Gaussian (see Fig.3(b), inset) and obtained an energy resolution R of 0.64. The p value calculated with Detect 2000 being 0.041, an estimation of the number of photons N generated at 5 MeV in the dye nano-composite is 400. For the dot nano-composite, no $\Delta E/E$ can be determined experimentally since no peak was detected. This result is in agreement with the simulations, which indicate that if an equivalent photon number N is inputted in the formula to calculate R , no energy resolution is expected. The comparison of the dot and dye systems constitutes a first step toward the understanding of the role played by the spectral properties of the dye and dot emitters in the scintillation output of these nano-composite systems. After inserting the wavelength-dependent PMT efficiency, and the lifetimes, the only major difference between the two systems is the Stokes shift, which is significantly smaller for the dots. We therefore attribute the output difference of these two systems to the Stokes shift, which govern the photon transport efficiency in the material.

Although the number of photons generated at 5 MeV in the present nano-composite systems is low (a commonly used scintillator material such as NaI produces about 30,000 photons at 1MeV), this number can change dramatically for thicker samples studied with penetrable gamma-rays. Moreover, the present systems have neither been optimized for loss minimization (reflective coating on all surfaces) nor for detection efficiency (APD instead of PMT).

Ultimately, simulations show that an energy resolution of about 2 % can be expected for these new quantum dot nano-composite materials due to their visible band gap. This approach would provide gamma-ray detectors with an energy resolution between the cooled semiconductor detectors and the inorganic scintillator crystals without any limitation on the area and volume of the detector and with room temperature operation. Our experimental results, coupled with simulations, demonstrated that in order to achieve this goal, the next step is to engineer the Stokes shift of semiconductor quantum dots. We will do this by using different materials such as PbS, or by anchoring organic chemical groups at the surface of the quantum dots.¹⁷

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REFERENCES

- ¹ C. B. Murray, D. J. Norris, and M. G. Bawendi, *J. Am. Chem. Soc.* **115**, 8706-8715 (1993).
- ² X. Peng, M. C. Schlamp, A. V. Kadavanich, and A. P. Alivisatos, *J. Am. Chem. Soc.* **119**, 7019-7029 (1997).
- ³ S. Kim, Y. T. Lim, E. G. Soltesz, A. M. De Grand, J. Lee, A. Nakayama, J. A. Parker, T. Mihaljevic, R. G. Laurence, D. M. Dor, L. H. Cohn, M. G. Bawendi, and J. V. Frangioni, *Nature Biotech.* **22**, 93-97 (2004).
- ⁴ I. L. Medintz, A. R. Clapp, H. Mattoussi, E. R. Goldman, B. Fisher, and J. M. Mauro, *Nature Materials* **2**, 630-638 (2003).
- ⁵ Y. Chan, J. S. Steckel, P. T. Snee, J.-M. Caruge, J. M. Hodgkiss, D. G. Nocera, and M. G. Bawendi, *Appl. Phys Lett.* **86**, 73102 (2005).
- ⁶ D. E. Persyk, M. A. Schardt, T. E. Moi, K. A. Ritter, and G. Muehllehner, *IEEE Trans. Nucl. Sci.* **27**, 168-171 (1980).
- ⁷ L. A. Andryushchenko, B. V. Grinev, A. M. Litichevskii, and L. V. Udovichenko, *Instruments and Experimental Techniques* **40**, 59-63 (1997).
- ⁸ M. Moszynski, M. Balcerzyk, W. Czarnacki, M. Kapusta, W. Klamra, P. Schotanus, A. Syntfeld, and M. Szawlowski, *IEEE Trans. Nucl. Sci.* **50**, 767-773 (2003).
- ⁹ W. H. Berninge, *IEEE Trans. Nucl. Sci.* **21**, 374-378 (1974).
- ¹⁰ M. Itaya, T. Inagaki, T. Iwata, G. I. Lim, H. Oishi, H. Okuno, Y. Tajima, H. Y. Yoshida, and Y. Yoshimura, *Nuclear Instruments & Methods in Physics Research A* **522**, 477-486 (2004).
- ¹¹ M. Akiba, M. Fujiwara, and M. Sasaki, *Optics Letters* **30**, 123-125 (2005).
- ¹² S. Dai, S. Saengerdsu, H.-J. Im, A. C. Stephan, and S. M. Mahurin, *AIP Conference Proceedings* **632**, 220-224 (2002).
- ¹³ J. F. Ziegler, J. P. Biersack, and U. Littmark, *The stopping and range of ions in solids*, Pergamon press, New York (1985).
- ¹⁴ G. F. Knoll, T. F. Knoll, and T. M. Henderson, *IEEE Trans. Nucl. Sci.* **35**, 872-875 (1988).
- ¹⁵ J. B. Birks, *The theory and practice of scintillation counting*, Pergamon Press, New York (1967).
- ¹⁶ P. Dorenbos, J. T. M. de Haas, and C. W. E. van Eijk, *IEEE Trans. Nucl. Sci.* **42**, 2190-2202 (1995).
- ¹⁷ A. Puzder, A. J. Williamson, J. C. Grossman, and G. Galli, *J. Am. Chem. Soc.* **125**, 2786-2791 (2003).

FIGURE CAPTIONS

FIG. 1. Characterization of the etched, cleaned, and dried porous glass matrix: a) SEM top views, without any conductive coating. b) Absorbance spectrum of a 1/16 inch thick slab.

FIG. 2. Absorbance and emission spectra of (a) porous glass impregnated with quantum dots, and (b) porous glass impregnated with Rhodamine B laser dye. Pictures of the devices are presented in inset.

FIG. 3. Background-subtracted scintillation output upon exposure to a $^{243-244}\text{Cm}$ source, recorded for 10 H, for (a) porous glass impregnated with quantum dots, and (b) porous glass impregnated with Rhodamine B dye. The peak recorded for the dye sample was fitted with a Gaussian curve (black line). The spectrum of the alpha source was measured using a Si(SB) detector and is presented in inset.

Figure 1

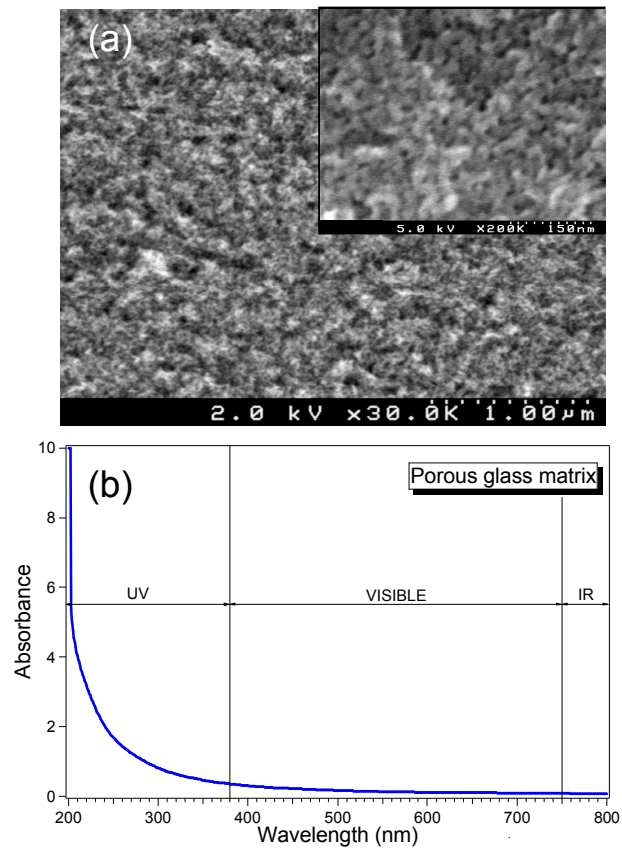


Figure 2

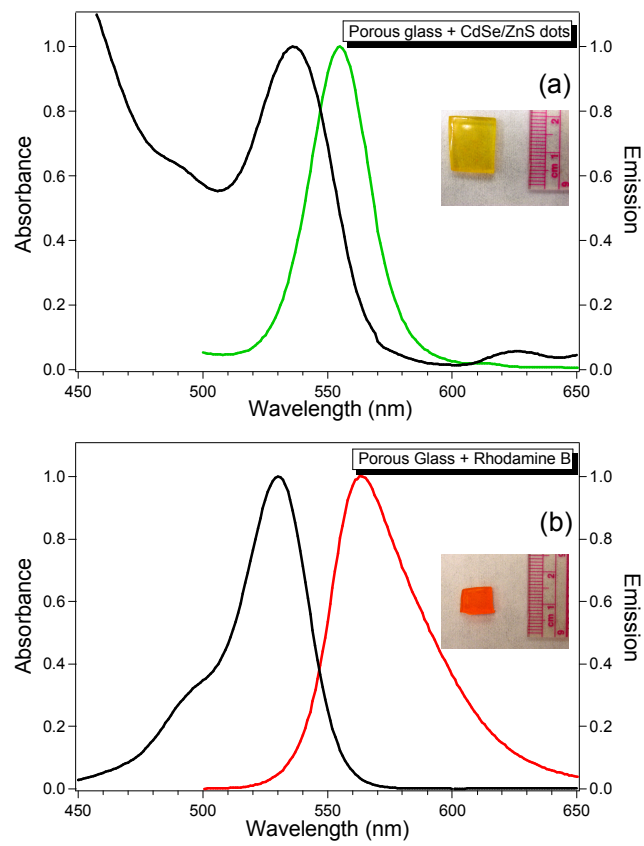


Figure 3

